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PB-271 732

Reactions of Isopropoxy Radicals with Nitrogen Oxides

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Prepared for:

Environmental Sciences Research Lab, Research Triangle Park, N C

Aug 77

PB 271 732

EPA-600/3-77-081
August 1977

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1 REPORT NO. EPA-600/4-77-081	3 RECIPIENT'S ACCESSION NO.
4 TITLE AND SUBTITLE: REACTIONS OF ISOPROPOXY RADICALS WITH NITROGEN OXIDES	5 REPORT DATE: August 1977
	6 PERFORMING ORGANIZATION CODE
7 AUTHOR(S): G. R. McMillan, M. J. Kaiserman	8 PERFORMING ORGANIZATION REPORT NO
9 PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106	10 PROGRAM ELEMENT NO. 1AA008 21ANC31 (FY 74) 11 CONTRACT/GRANT NO. R-800629
12 SPONSORING AGENCY NAME AND ADDRESS: Environmental Sciences Research Laboratory - RTP, NC, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711	13 TYPE OF REPORT AND PERIOD COVERED: Final 14 SPONSORING AGENCY CODE: EPA/600/09

15 SUPPLEMENTARY NOTES

16 ABSTRACT

Information was sought concerning reactions of isopropoxy radicals with nitric oxide and nitrogen dioxide. Isopropyl nitrate was photodissociated in the presence of oxides of nitrogen and an inert gas. The reaction was found to be less important than the alkoxy radical NO reactions. The ratio of disproportion to recombination of isopropoxy and NO was found to be smaller than the published value (0.12 versus .15).

17 KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Photochemical reactions *Nitrogen oxides *Reaction kinetics		13B 07B 07E 07D

18 DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19 SECURITY CLASS (This Report): UNCLASSIFIED	21 NO. OF PAGES: 38
	20 SECURITY CLASS (This page): UNCLASSIFIED	22 PRICE: $3.00 A01

EPA Form 2220-1 (9-73)

EPA-600/3-77-081
August 1977

Reactions of Isopropoxy Radicals with Nitrogen Oxides

by

G. R. McMillan
M. J. Kaiserman
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Grant No. R800659

Project Officer

J. J. Bufalini
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, N. C. 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ABSTRACT

Information about the reactions of isopropoxy radicals with nitrogen dioxide and nitric oxide was sought in an investigation of the gas-phase co-photolysis of isopropyl nitrite and nitrogen dioxide. Mixtures of these two compounds and mixtures of those two compounds with added inert gas were illuminated in small quartz cylinders and in a long path infrared gas cell. Certain rate constant ratios were calculated from the quantum yields and product distribution on the basis of a partial mechanism.

Alkoxy radicals with α-hydrogen atoms are believed to react with nitrogen dioxide by two processes. Combination occurs yielding an alkyl nitrate. A parallel process, disproportionation, yields a carbonyl compound and nitrous acid. Comparing the present results with literature values for the relative probability of these two processes shows that disproportion of isopropoxy and nitrogen dioxide is considerably less important than expected from the general appreciation of alkoxy/nitrogen dioxide reactions.

Re-evaluation of some published results in the light of the present findings suggests that the quantum yields of photodissociation of alkyl nitrites are likely to be greater than currently accepted values and that disproportionation of alkoxy radicals with nitric oxide is probably less important than is currently accepted.

This report was submitted in fulfillment of Grant Number R800659 by Case Western Reserve University under partial sponsorship of the Environmental Protection Agency. Work was completed as of June, 1976.

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ACKNOWLEDGMENTS

Case Western Reserve University provided support and assistance for this work in several ways. Thanks are also due to Dr. A. J. Gumodi for consultation on infrared techniques and to Mr. C. S. Kan for his experiments on generation of thermally-equilibrated alkoxy radicals.

SECTION I

INTRODUCTION

For alkoxy radicals possessing an alpha hydrogen, the expected reactions with nitrogen dioxide are disproportionation and recombination.[1]

$$R'RCHO\cdot + NO_2 \xrightarrow{k_d} R'RCO + HNO_2 \qquad \text{Disproportionation}$$

$$R'RCHO\cdot + NO_2 \xrightarrow{k_r} R'RCHONO_2 \qquad \text{Recombination}$$

Neither these nor other gas-phase reactions of alkoxy radicals have been studied using a direct detection method, and in fact few absolute rate constants of alkoxy radicals are available. No value for k_d or k_r is known to within a factor of about 100.[2] On the other hand, k_d/k_r ratios should be determinable by use of methods now available. The rate constant, k_r, can be calculated in principle by using the method of Benson,[3] but the kinetic information needed for such a calculation is not always available. These ratios are also directly useful for kinetic analysis of other reaction systems.[4] For photochemical smog formation, the ratio is of interest because disproportionation, unlike recombination, is not likely to be chain terminating.[5] The data available for the ratio k_d/k_r are collected in Table I.

The state of knowledge of these ratios is unsatisfactory. Although alkyl peroxides are considered to be suitable sources of alkoxy radicals, there are clearly problems in using these alkoxy radical sources in the nitrogen dioxide reaction. One such problem may be surface effects similar to those reported by Ludwig for pyrolysis of isopropyl peroxide-nitric mixtures.[6] In any case, for application to smog formation, it is desirable to have k_d/k_r values for ambient temperatures. Demerjian, Kerr, and Calvert use k_d/k_r values of 0.1 and 0.2 for various alkoxy radicals in their detailed computer model of smog formation.[5]

It was decided to study the isopropoxy-nitrogen dioxide system at room temperature. Isopropoxy was selected for the following reasons. First, no study had yet been made of secondary alkoxy radical-nitrogen dioxide systems. Second, as demonstrated by Ludwig, isopropoxy could be produced from isopropyl nitrite in a clean photochemical reaction at 3660 Å.[6]

The only primary dissociative process of isopropyl nitrite upon absorption of radiation of 3660 Å wavelength is (1), where α is the fraction of excited isopropoxy radicals.

TABLE 1. VALUES OF k_d/k_r FOR REACTIONS OF ALKOXY RADICALS WITH NITROGEN DIOXIDE

Radical	Temperature, °C	Source		k_d/k_r	Ref.
$CH_3O\cdot$	25	CH_3ONO	Photolysis	0.1 ± 0.1^a	7
	121	$(CH_3O)_2$	Pyrolysis	$0.23-0.75^a$	2
	130	$(CH_3O)_2$	Pyrolysis	0.10^b	8
	163	$(CH_3O)_2$	Pyrolysis	$0.05-1.65^a$	2
$CH_3CH_2O\cdot$	132	$(CH_3CH_2O)_2$	Pyrolysis	0.46^b	8

a. Calculated by author from reported values of $k_r/(k_r+k_d)$.

b. No reasonable error limits may be assigned as these values are based on results obtained from three and two experiments respectively.

$$(CH_3)_2CHONO \xrightarrow{h\nu} \alpha(CH_3)_2CHO^{\bullet *} + (1-\alpha)(CH_3)_2CHO^{\bullet} + NO \qquad (1)$$

there is evidence that the alkoxy radicals produced behave chemically as if there were two types present -- a vibrationally-excited radical and a radical at thermal equilibrium.[7,10] At low pressures, all or nearly all the excited isopropoxy radicals dissociate according to step (2).[8]

$$(CH_3)_2CHO^{\bullet *} \xrightarrow{k_2} CH_3COH + CH_3^{\bullet} \qquad (2)$$

Unexcited isopropoxy radicals will undergo a complex sequence of secondary reactions.[11,12] However, if photolysis occurs in the presence of an excess of nitric oxide, this complex sequence of secondary reactions can be reduced. All the unexcited isopropoxy radicals will be scavenged as described by the disproportionation, equation (3), and recombination, equation (4), steps.[8,13]

$$(CH_3)_2CHO^{\bullet} + NO \xrightarrow{k_3} CH_3COCH_3 + HNO \qquad (3)$$

$$(CH_3)_2CHO^{\bullet} + NO \xrightarrow{k_4} (CH_3)_2CHONO \qquad (4)$$

The rate constant ratio, k_3/k_4, independent of temperature, has been reported to be as low as 0.15 and as high as 0.22.[10-12]

When isopropyl nitrite is photolyzed in the presence of nitrogen dioxide, the isopropoxy radicals are expected to react as follows:[7,8]

$$(CH_3)_2CHO^{\bullet} + NO_2 \xrightarrow{k_5} CH_3COCH_3 + HNO_2 \qquad (5)$$

$$(CH_3)_2CHO^{\bullet} + NO_2 \xrightarrow{k_6} (CH_3)_2CHONO_2 \qquad (6)$$

With $(k_5 + k_6)$ likely to be greater than or equal to $10^{9.5}$ l/mole-sec,[8] no other reactions of unexcited isopropoxy are expected to be important at early stages of the photolysis provided that the concentration of nitrogen dioxide is not too low. If acetone and isopropyl nitrate are formed only in steps (5) and (6), and if no subsequent removal of the products occurs, and if certain other conditions are met, then $R_{CH_3COCH_3} = k_5[NO_2][(CH_3)_2CHO^{\bullet}]$ and $R_{(CH_3)_2CHONO_2} = k_6[NO_2][(CH_3)_2CHO^{\bullet}]$. This leads to:

$$\frac{[CH_3COCH_3]_t}{[(CH_3)_2CHONO_2]_t} = \frac{k_5}{k_6} \qquad (A)$$

The concurrent photolysis of nitrogen dioxide complicates this simple analysis. The extinction coefficient of this compound at 3660 Å is about 155 l/mole-cm,[14] compared with approximately 50 l/mole-cm for isopropyl nitrite.[15] Leighton gives a detailed description of the photochemistry of nitrogen dioxide.[14] The main steps at wavelengths shorter than 3980 Å are:

$$NO_2 \xrightarrow{h\nu} NO + O(^3P) \qquad (7)$$

$$O(^3P) + NO_2 \xrightarrow{k_8} NO + O_2 \quad (8)$$

$$O(^3P) + NO_2 + M \xrightarrow{k_{8'}} NO_3 + M \quad (8')$$

Since the primary quantum yield is 0.95,[59] nitrogen dioxide will photodecompose efficiently under the proposed conditions. In view of the products of this photodecomposition, at least two additional steps which form acetone must be considered.[57,74]

$$(CH_3)_2CHCHO + O(^3P) \xrightarrow{k_9} CH_3COCH_3 + NO + HO \cdot \quad ? \quad (9)$$

$$(CH_3)_2CHO \cdot + O_2 \xrightarrow{k_{10}} CH_3COCH_3 + HO_2 \cdot \quad (10)$$

If the ratio k_9/k_8 is to be simply extracted, the constraints of the system place the following limits on the range of pressures of nitrogen dioxide at which the system may be studied:

1. The pressure of nitrogen dioxide must be high enough to scavenge the isopropoxy radicals in order to avoid the formation of acetone and isopropyl nitrate through reactions of isopropoxy other than (8) and (8').

2. The pressure of nitrogen dioxide must be high enough to avoid depletion in the reaction zone.

3. The pressure of nitrogen dioxide must be low enough to avoid appreciable photolysis which would lead to significant product formation through reactions (9) and (10).

4. The pressure of nitrogen dioxide must be low enough to minimize product-forming reactions of nitrogen tetroxide, which is formed in the nitrogen dioxide-nitrogen tetroxide equilibrium.

The results of the experiments to determine k_9/k_8 (k_9/k_7) may also lead to an independent check of the published value of the primary quantum yield for dissociation of isopropyl nitrite, which is the only value available for this or any secondary alkyl nitrite. Ludwig reported ϕ_1 to be 0.36 at 26°C and at 3660 Å on the basis of product yields and a proposed mechanism for the isopropyl nitrite-nitric oxide system.[57] This method requires accurate knowledge of the ratio of k_2/k_4. If k_2/k_4 is as low as 0.15[75] or as high as 0.22,[76] ϕ_1 can vary from 0.40 to 0.36. The primary quantum yield also requires accurate measurement of a minor product, acetone($\Phi_{CH_3COCH_3} = 0.060$).[57]

A confirmation of the value for the primary yield ϕ_1 reported by Ludwig seems desirable. For the isopropyl nitrite-nitrogen dioxide system, consideration of reactions (2), (5) and (6) leads to:

$$\phi_1 I_a = k_2[(CH_3)_2CHO \cdot] + (k_5 + k_6)[(CH_3)_2CHO \cdot][NO_2] \quad (B)$$

$$\phi_1 = \Phi_{CH_3CHO} + (1 + k_5/k_6)\Phi_{(CH_3)_2CHONO} \quad (C)$$

Acetaldehyde is no more than a trace product,[17] thus the determination of ϕ_1 requires the accurate measurement of k_3/k_5 as well as the quantum yield of isopropyl nitrate formation. If ϕ_1 can be obtained, Ludwig's data may be re-interpreted to give a new value of k_3/k_5.

In summary, several reasons led to the decision to study the photolysis of isopropyl nitrite in the presence of nitrogen dioxide.

1. No detailed information is available for reactions of secondary alkoxy radicals with nitrogen dioxide. Furthermore, no value of k_d/k_p for any alkoxy radical is well established.

2. Alkyl nitrites are a good source of alkoxy radicals and the methods developed in this study can be extended to primary as well as other secondary alkoxy radicals.

3. The result obtained for the primary quantum yield will be a good check of the value obtained by Ludwig from the photolysis of isopropyl nitrite-nitric oxide mixtures. Ludwig's data may then be reinterpreted on the basis of the new primary quantum yield.

SECTION 4

CONCLUSIONS

The importance of the disproportionation reaction between the isopropoxy radical and nitrogen dioxide is less than would be expected from literature data on alkoxy radical/nitrogen dioxide reactions. The ratio of rate constants for disproportionation and combination of isopropoxy and nitric oxide is found to be smaller than any of the five literature values.

Alkoxy radical/NO_2 reactions usually have been studied using alkyl peroxides as thermal or photochemical radical sources. If the present study is supported by further work, the peroxide technique and results obtained using the peroxide technique will have to be reconsidered carefully. Most literature data on the photolysis rates of alkyl nitrites must be recalculated.

SECTION 5

RECOMMENDATION

None of the reactions discussed in this report are believed to be critical in smog formation nor in laboratory smog chamber processes, at least under most conditions. These reactions and their rate constants do appear in a generalized way in most reaction sets used for computer simulations of smog. Appropriate modification of rate constant input should be considered.

SECTION 4

EXPERIMENTAL

MATERIALS

Isopropyl nitrite was prepared by reaction of isopropyl alcohol with nitrous acid. The product was treated with anhydrous K_2CO_3 and distilled at atmospheric pressure. Nitrogen dioxide from the Matheson Chemical Company was passed over P_2O_5 and fractionally distilled. Both isopropyl nitrite and the nitrogen dioxide were stored on the vacuum line at -78° in the dark. Nitrogen was passed over hot copper to remove oxygen and through traps cooled to -196° to remove condensable impurities.

APPARATUS

Conventional mercury-free high vacuum lines were used for storage, sample preparation, and preliminary separation.

The source of 3660 Å radiation was a Hanovia 673A medium pressure mercury arc, used with a Corning 7-37 filter in order to reproduce the spectral intensity distribution realized by Ludwig.[7] The reaction cell used for quantum yield measurements was a quartz cylinder, 10-cm long, with planar end faces. Reactants were allowed to mix in the cell by diffusion. The absorbed light intensity, based on ferrioxalate actinometry was integrated over the course of an illumination. Depending upon relative pressure, the intensity of light absorbed by nitrogen dioxide was 2-12% of that absorbed by isopropyl nitrite.

Photolysis experiments with a long-path gas cell allowed in situ analysis of the reaction mixture by infrared spectrophotometry (LPIR). The aluminum cell, obtained from Beckman Instruments, Inc., has a volume of 12.5 and an optical path variable between 0.1 and 20 m. Photolysing light enter the cell through quartz windows. The light source and filter used was the same as that used in the small cell experiments.

ANALYSIS

The reaction mixture from photolyses in the small cell was analyzed by gas chromatography on a 1-m long, 0.6 cm o.d. stainless steel column containing 20% tricresyl phosphate on Chromasorb W. The reaction mixture was transferred on the vacuum line to a thin capillary. The sample was injected into the chromatograph by breaking the capillary in a teflon tube through which carrier gas was flowing.

In the i-PrONO$_2$ experiments, isopropyl nitrate was measured from the absorbance at 1282 cm^{-1}. Acetone was measured from the total carbonyl absorbance at 1742 cm^{-1} by subtracting the contribution from acetaldehyde, using quantum yield data of Ludwig.[7]

SECTION 5

RESULTS

THE REACTION IN SMALL QUARTZ CELLS

Illumination of mixtures of isopropyl nitrite vapor and nitrogen dioxide in small cells led to three carbon-containing products detectable by gas chromatography and/or long-path infrared spectrophotometry-acetone, acetaldehyde and isopropyl nitrate.

Reproducible yields of the carbonyl products were not obtained by gas chromatography. Large, irreproducible amounts of acetone were observed in the absence of light. Exhaustive tests, with variation in the analytical procedure, failed to provide a solution to the interference. It was concluded that acetone is formed by thermal processes upon condensation of the reaction mixture in the vacuum line and in the first section of the GC column.

The quantum yields of isopropyl nitrate appear in Tables 2 and 3. The photolyses, of 2.5-min duration, were done in the 10-cm cell at a temperature of 25°. The percent conversion of isopropyl nitrite was kept constant at approximately 0.06%, but the percent conversion of nitrogen dioxide was as high as 10% for small initial concentrations of this reactant.

The data in Table 2 illustrate the effect of changing the concentrations of the components of the photolysis mixture. The variation of the pressure of either isopropyl nitrite or nitrogen dioxide produced no significant change in the results. The average quantum yield of isopropyl nitrate is 0.54 ± 0.02 (s.d.).

The data in Table 3 show the effect of the addition of an inert gas, nitrogen, to photolysis mixtures of constant nitrogen dioxide pressure and varying isopropyl nitrite pressures. The quantum yields were not significantly different from those measured for the nitrogen-free case.

A number of experiments were carried out in which mixtures of isopropyl nitrite (at about 7.0 Torr) and the nitric oxide (at about 30-40 Torr) were illuminated for 6 hrs. The quantum yields of acetone were: 0.040, 0.046, 0.046, 0.038, and 0.036. Isopropyl nitrate was also observed in trace amounts with quantum yields in the range of 0.001-0.002.

TABLE 2. QUANTUM YIELDS OF ISOPROPYL NITRATE

$P_{(CH_3)_2CHONO}$, Torr	P_{NO_2}, Torr	10^{-15} I_a, Quanta sec^{-1}	$\Phi_{(CH_3)_2CHONO_2}$
7.2	0.57	0.35	0.56
7.3	0.57	0.34	0.54
7.4	0.29	0.38	0.52
7.6	0.29	0.37	0.57
7.7	0.29	0.40	0.53
7.3	0.14	0.37	0.52
7.6	0.14	0.37	0.51
7.9	0.07	0.38	0.52
7.7	0.07	0.31	0.56
3.8	0.14	0.20	0.57
3.9	0.14	0.20	0.54
3.9	0.14	0.21	0.54
1.8	0.14	0.10	0.54
1.7	0.14	0.09	0.55
1.9	0.14	0.10	0.50

TABLE 5. QUANTUM YIELDS OF ISOPROPYL NITRATE IN THE PRESENCE OF NITROGEN

$P_{(CH_3)_2CHONO}$, Torr	P_{NO_2}, Torr	P_{N_2}, Torr	10^{-15} I_a, Quanta sec^{-1}	$\Phi_{(CH_3)_2CHONO_2}$
7.6	0.14	36	0.34	0.51
7.0	0.14	25	0.34	0.54
5.9	0.14	42	0.20	0.50
5.8	0.14	24	0.22	0.58
1.9	0.14	8	0.08	0.52
1.8	0.14	12	0.09	0.51

THE REACTION IN THE LONG PATH INFRARED (LPIR) CELL

No dark reactions were observed. The results of photolysis of isopropyl nitrite/nitrogen dioxide/nitrogen mixtures at 25° are shown in Table 4. The ratio of yields $Y_{CH_3COCH_3}/Y_{(CH_3)_2CHONO}$ is found to be constant, all values falling in the range 0.06 ± 0.01 with variation in isopropyl nitrite pressure (1.5-6.8 Torr), nitrogen dioxide pressure (0.08-0.78 Torr), and nitrogen pressure (3-580 Torr).

Table 5 shows the results from photolysis of isopropyl nitrite/nitrogen dioxide mixtures. No nitrogen or other inert gas was present. The yield ratio was unaffected by halving the photolysis time at a constant pressure of nitrogen dioxide. This effect was observed at a nitrogen dioxide pressure of 0.20 Torr at times of 10.0 and 5.0 min and at a nitrogen dioxide pressure of 0.15 Torr at times of 5.0 and 2.5 min. The yield ratio was also unaffected by a five-fold change of nitrogen dioxide pressure at a constant isopropyl nitrite pressure of 6.7 Torr and a constant photolysis time of 2.5 min. There was, however, a change in the yield ratio when the pressure of nitrogen dioxide was held constant and the pressure of isopropyl nitrite was decreased below a certain level. At isopropyl nitrite pressures of 6.7 and 6.8 Torr, the same yield ratio was observed as in the presence of added nitrogen, but at pressures of isopropyl nitrite of 4.8 Torr and below, the yield ratio decreased with decreasing pressure. This decrease of the yield ratio was observed at pressures of nitrogen dioxide of 0.15 and 0.08 Torr. Furthermore, at a given low pressure of isopropyl nitrite, the yield ratio was about the same for the two pressures of nitrogen dioxide.

TABLE 4. PRODUCT YIELDS IN THE PRESENCE OF NITROGEN FROM PHOTOLYSES IN THE IN THE INFRARED GAS CELL

$P_{(CH_3)_2CHONO}$, Torr	P_{NO_2}, Torr	P_{N_2} Torr	$Y^a_{CH_3COCH_3}$, Micromol	$Y^a_{(CH_3)_2CHOHO_2}$, Micromol	$\frac{Y_{CH_3COCH_3}}{Y_{(CH_3)_2CHONO_2}}$
6.8	0.08	350	0.84	13	0.07
6.8	0.08	180	0.60	13	0.05
6.8	0.08	130	0.67	10	0.07
6.8	0.08	84	0.61	11	0.06
4.8	0.08	150	0.57	7.8	0.05
4.7	0.08	110	0.50	8.8	0.06
3.8	0.08	560	0.34	5.0	0.06
3.8	0.08	110	0.42	7.4	0.06
3.8	0.08	90	0.43	6.4	0.07
3.8	0.08	3	0.37	7.8	0.05
1.5	0.08	18	0.14	2.9	0.05
1.5	0.08	18	0.15	2.7	0.06
1.5	0.08	18	0.15	3.1	0.05
1.5	0.08	18	0.23	3.4	0.07
6.7	0.47	11	0.46	9.7	0.05
6.8	0.47	13	0.67	12.0	0.06
6.8	0.78	11	0.63	9.5	0.07
6.8	0.78	11	0.43	6.4	0.07
3.8	0.26	15	0.47	8.9	0.05
3.8	0.26	15	0.60	9.0	0.07

[a]Product yields from photolysis of 2.5 min duration.

TABLE 8. PRODUCT YIELDS IN THE ABSENCE OF NITROGEN FROM PHOTOLYSES IN THE INFRARED GAS CELL

Photolysis Time, min	$P_{(CH_3)_2CHONO}$, Torr	P_{NO}, Torr	$V^a_{CH_3COCH_3}$, Micromol	$V^a_{(CH_3)_2CHONO_2}$, Micromol	$\frac{V_{CH_3COCH_3}}{V_{(CH_3)_2CHONO_2}}$
10	6.8	0.30	3.0	52	0.06
10	6.8	0.30	3.1	55	0.06
10	6.8	0.28	3.8	49	0.08
10	6.7	0.29	3.3	58	0.06
10	6.7	0.29	2.9	63	0.05
10	6.7	0.29	2.6	55	0.05
5	6.7	0.15	1.4	25	0.06
5	6.7	0.15	1.4	25	0.06
5	6.7	0.15	1.5	22	0.06
5	6.7	0.15	1.8	23	0.08
5	6.7	0.15	1.9	25	0.08
5	6.7	0.28	2.1	32	0.07
2.5	6.8	0.15	0.75	16	0.05
2.5	6.8	0.15	0.75	16	0.05
2.5	6.8	0.15	1.0	18	0.06
2.5	6.7	0.08	0.72	15	0.05
2.5	6.7	0.08	0.72	15	0.05
2.5	6.7	0.08	0.81	14	0.06
2.5	6.7	0.59	0.95	20	0.05
2.5	6.7	0.58	1.0	16	0.06
2.5	6.6	0.15	0.88	19	0.05

(continued)

TABLE 6. (continued)

Photolysis Time, min	$P_{(CH_3)_2CHCHO}$, Torr	P_{NO_2}, Torr	$Y^a_{CH_3COCH_3}$, Micromol	$Y^a_{(CH_3)_2CHCHO_2}$, Micromol	$\frac{Y_{CH_3COCH_3}}{Y_{(CH_3)_2CHCHO_2}}$
2.5	8.8	0.15	0.72	15	0.05
2.5	4.8	0.15	0.41	11	0.04
2.5	4.8	0.15	0.55	13	0.04
2.5	5.4	0.15	0.25	9.5	0.03
2.5	5.4	0.15	0.25	9.5	0.03
2.5	8.8	0.08	0.67	14	0.05
2.5	8.8	0.08	0.68	14	0.05
2.5	4.8	0.08	0.33	13	0.03
2.5	4.7	0.08	0.27	9.6	0.03
2.5	5.8	0.08	0.23	8.5	0.03
2.5	5.8	0.08	0.16	9.7	0.02
2.5	5.4	0.05	0.23	8.5	0.03
2.5	5.4	0.08	0.27	9.6	0.03
2.5	2.8	0.08	0.13	7.4	0.02
2.5	2.8	0.08	0.13	7.7	0.02

[a]Product yields from photolysis of 2.5 min duration

SECTION 6

DISCUSSION

PRELIMINARY DISCUSSION OF THE MECHANISM

Of the many elementary chemical processes which are expected to be involved in the photolysis of isopropyl nitrite - nitrogen dioxide mixtures at 3660 Å, the following need to be considered if the results are to be interpreted.

$$(CH_3)_2CHONO \xrightarrow{h\nu} \alpha(CH_3)_2CHO\cdot^{\phi} + (1-\alpha)(CH_3)_2CHO\cdot + NO \qquad (1)$$

$$(CH_3)_2CHO\cdot^{\phi} \xrightarrow{k_2} CH_3CHO + CH_3\cdot \qquad (2)$$

$$(CH_3)_2CHO\cdot + NO \xrightarrow{k_3} CH_3COCH_3 + HNO \qquad (3)$$

$$(CH_3)_2CHO\cdot + NO \xrightarrow{k_4} (CH_3)_2CHONO \qquad (4)$$

$$(CH_3)_2CHO\cdot + NO_2 \xrightarrow{k_5} CH_3COCH_3 + HNO_2 \qquad (5)$$

$$(CH_3)_2CHO\cdot + NO_2 \xrightarrow{k_6} (CH_3)_2CHONO_2 \qquad (6)$$

$$NO_2 \xrightarrow{h\nu} NO + O(^3P) \qquad (7)$$

$$O(^3P) + NO_2 \xrightarrow{k_8} NO + O_2 \qquad (8)$$

$$O(^3P) + NO_2 + M \xrightarrow{k_{8'}} NO_3 + M \qquad (8')$$

$$(CH_3)_2CHONO + O(^3P) \xrightarrow{k_9} \text{---} \longrightarrow CH_3COCH_3 + NO + HO\cdot\ ? \qquad (9)$$

$$(CH_3)_2CHO\cdot + O \xrightarrow{k_{10}} CH_3COCH_3 + HO_2\cdot \qquad (10)$$

Other processes would have to be considered if the extent of reaction was greater than perhaps 1%. Under the scavenging conditions of the experiments, bimolecular reactions involving isopropoxy or oxygen atoms having activation energies greater than about 3 kcal/mole should be too slow to compete.

Steps (1) and (7)

Reaction (1) is generally accepted as the only primary dissociative process in the photolysis of alkyl nitrites.[1] Discussion of the possible effect of nitrogen dioxide on the probability of this process is deferred. Step (7) will occur concurrently with step (1). However, the relative rates of these

photodecompositions may be varied by changing the ratio of concentrations of nitrogen dioxide to isopropyl nitrite. Thus the rate of (7) is calculated to be 3-23% of the rate of (1) in the various experiments.

Step (2)

This is a minor process shown by Ludwig to occur at about 9% of the rate of step (1). Nitric oxide is an inefficient quencher of excited isopropoxy.[17] Even if nitrogen dioxide is highly efficient, there would be no great change in the steady-state concentration of isopropoxy.

Steps (3) and (4)

These are established reactions at high nitric oxide pressures,[17] but they should not become important in the present system until nitric oxide formed in reactions (1), (7), and (8) has built up to appreciable concentrations after long photolysis times.

Steps (5) and (6)

As $k_5 + k_6 \approx 10^{10}$ ℓ/mole-sec, these are likely to be the principal initial fates of isopropoxy radicals at nitrogen dioxide pressures greater than 0.05 torr.

Steps (8), (8') and (9)

Demerjian, Kerr, and Calvert report that $k_8 = 5.3 \times 10^9$ ℓ/mole-sec at 25° C.[5] Step (8') will always accompany step (8) with the relative rates depending on the nature and pressure of the third body present. No information is available in the literature about reactions of nitrogen trioxide with alkyl nitrites, but the presence of this intermediate cannot be ignored a priori. The possible effects of nitrogen trioxide in the system will be discussed later.

No data are available for step (9), but acetone seems to be a likely ultimate product.[24] From the data of Davidson and Thrush, the rate constant for the reactions of $O(^3P)$ with ethyl nitrite is calculated to be 7.65×10^8 ℓ/mole-sec at 25°C.[24] Assuming the same value for k_9, it can be estimated that, in the experiments in which acetone was measured, the rate of step (9) was 25% of the rate of step (8) at the highest ratio of isopropyl nitrite to nitrogen dioxide and 5% of the rate of step (8) at the lowest ratio. Based on these calculations, the question of a possible contribution of step (9) to acetone formation must be left open.

Step (10)

Heicklen estimates that the rate constant of the reaction of molecular oxygen with methoxy is $10^{7.2}$ ℓ/mole-sec.[25] Assuming the same value for k_{10}, a comparison of rates of steps (10) and (5) shows that the contribution of step (10) to the formation of acetone is negligible.

The discussion and interpretation of the acetone and isopropyl nitrate

yields will be organized around steps (1) - (5). The possible influence of the other processes will be discussed later.

ESTIMATE OF k_3/k_5

The mechanism predicts that, for small extents of reaction, the yield ratio (acetone/isopropyl nitrate) should be independent of irradiation time, nitrogen dioxide pressure, isopropyl nitrite pressure, and inert gas pressure. Indeed, the yield ratio was 0.06 ± 0.01 (s.d.), independent of all parameters except isopropyl nitrite pressure. In the absence of added nitrogen the limiting value 0.06 was found only at 6.8 and 8.8 Torr of isopropyl nitrite. As seen in Table 5, the yield ratio decreases at lower isopropyl nitrite pressures, reaching 0.02 at 2.8 Torr of isopropyl nitrite.

When nitrogen is initially present in the reaction mixture, the yield ratio reaches the limiting value even at low isopropyl nitrite pressures (Table 4). Comparison of data in Tables 4 and 5 shows that the acetone yield is normal at low isopropyl nitrite pressures, and that the decrease in the yield ratio is due to the apparent extra production of isopropyl nitrate. This effect is unanticipated, and no explanation for it can be advanced with confidence. Any such explanation must take into account the following two observations. First, a pressure of nitrogen as low as 5 Torr is sufficient to give the high-pressure limiting value of the yield ratio. Second, no decrease in the quantum yield of isopropyl nitrate is observed in the small cell.

The limiting value of the yield ratio, 0.06 ± 0.01 (s.d.), is assigned to the ratio of rate constants k_3/k_5.

PRIMARY DISSOCIATIVE QUANTUM YIELD OF ISOPROPYL NITRITE

Assuming that for short duration photolyses steps (2), (5), and (6) account for the isopropoxy radicals generated in Step (1), the primary dissociative yield, ϕ_1, is given by:

$$\phi_1 = \phi_{CH_3CHO} + (1 + k_3/k_5)\phi_{(CH_3)_2CHONO_2} \qquad (C)$$

$$= 0.031 + (1 + 0.06)(0.54)$$

$$= 0.60 \pm 0.03$$

The acetaldehyde yield is that obtained by Ludwig.[5,17]

The experimental primary quantum yield is much greater than the value of 0.36 calculated by Ludwig from results of photolyses of mixtures of isopropyl nitrite and nitric oxide at 26°C and 3660 Å.[17] In that work, isopropoxy radicals were proposed to disappear via steps (2), (3), and (4). The primary dissociative yield was calculated from:

$$\phi_1 = \phi_{CH_3CHO} + (1 + k_3/k_4)\phi_{CH_3COCH_3} \qquad (D)$$

If the Ludwig mechanism is correct and if ϕ_1 is much greater than reported by Ludwig, the main source of error is likely to lie either in $\phi_{CH_3COCH_3}$ or

k_3/k_4.

$$(CH_3)_2CHO\cdot + NO \xrightarrow{k_3} CH_3COCH_3 + HNO \quad (3)$$

$$(CH_3)_2CHO\cdot + NO \xrightarrow{k_4} (CH_3)_2CHONO \quad (4)$$

During the course of the present study, a few attempts were made to reproduce the value of $\Phi_{CH_3COCH_3}$ obtained by Ludwig.[17] Values about 30% lower were obtained. This change in value is in the wrong direction to explain the discrepancy in ϕ_1 and probably reflects the difficulty in analysing for a compound both produced in small yield and present as an impurity in the starting material. The yields obtained by Ludwig should be considered the more reliable.

If the value for $\Phi_{CH_3COCH_3}$ determined by Ludwig is correct, then according to equation C, k_3/k_4 would be 0.12 if ϕ_1 is 0.60. The published values of k_3/k_4 obtained from studies of the photolysis and pyrolysis of isopropyl peroxide - nitric oxide mixtures are presented in Table 6. The value of 0.12 is outside the range of reported values but not much so.

TABLE 6. RATE CONSTANT RATIOS (k_3/k_4) OF ISOPROPOXY AND NITRIC OXIDE

Radical Source	k_3/k_4	T°C	Ref.
Photolysis(2300-2500Å)	0.15	26,77	14
Pyrolysis	0.15	121-159	15
Pyrolysis	0.21	104-149	16
Pyrolysis	0.22	126-180	17

Neither the pyrolysis nor the photolysis systems is without complication. Ludwig observed a surface contribution towards production of acetone at temperatures below 150°C.[17] If, in the pyrolysis of isopropyl peroxide - nitric oxide mixtures, some isopropyl nitrite produced by step (4) undergoes this surface catalysed conversion, the apparent k_3/k_4 will be too high. It should be noted that ratios of rate constants $k_{disproportionation}/k_{combination}$, if in error, are expected to be too high. This is because there are several side reactions that may form the disproportionation product, but few that may form the combination product. All published values of k_3/k_4 were obtained from results of systems wherein isopropoxy was formed by photolysis or pyrolysis of isopropyl peroxide. It is suggested on the basis of the present study that all these values (including two published by the principal investigator) are too high. This further suggests that there is some problem with the peroxide method. Since nearly all information about disproportionation and combination of alkoxy radicals and NO_2 are based on the use of peroxides as radical sources,

it is concluded that published $k_{disproportionation}/k_{combination}$ ratios must be accepted only with serious reservations.

POSSIBLE INFLUENCE OF OTHER REACTIONS ON THE VALUE REPORTED FOR k_5/k_6

Influence of Nitrogen Dioxide on the Primary Dissociative Yield of Isopropyl Nitrite

It has been assumed that the primary dissociative yield of isopropyl nitrite is not affected by the presence of nitrogen dioxide. The data seem to support this assumption. Simple quenching of electronically excited isopropyl nitrite molecules is ruled out by the lack of variation of the quantum yield of isopropyl nitrite with change in nitrogen dioxide pressure. Indeed, there seems to be no evidence in the literature for quenching of excited alkyl nitrite molecules by any molecule. High quantum yields have been calculated for photolysis of n-octyl nitrite in solution.[58] Ludwig observed no quenching by nitric oxide at pressures up to 40 Torr.[17] More to the point, in view of the high dissociative quantum yield observed in this study, there is the possibility of some reaction such as (11), which might produce isopropoxy radicals.

$$(CH_3)_2CHONO^* + NO_2 \xrightarrow{k_{11}} (CH_3)_2CHO^\cdot + N_2O_3 \qquad (11)$$

This reaction is somewhat analogous to the well-known process:[57,58]

$$(CH_3)_2CONO + CH_3^\cdot \longrightarrow (CH_3)_2CO^\cdot + CH_3NO$$

Step (11) can probably be excluded, however, in light of the observed lack of dependence of the quantum yield of isopropyl nitrate on nitrogen dioxide pressure.

Influence of Nitrogen Trioxide

As previously stated, no account can be given of the fate of nitrogen trioxide formed in the process (8'), which always will proceed concurrently with process (8).

$$O(^3P) + NO_2 \xrightarrow{k_8} NO + O_2 \qquad (8)$$

$$O(^3P) + NO_2 + M \xrightarrow{k_{8'}} NO_3 + M \qquad (8')$$

On the basis of bond energy and activation energy correlations, Demerjian, Kerr, and Calvert predict k_{11} to be about 2.5×10^5 l/mole-sec.[7] If the rate constant for nitrogen trioxide reacting with isopropyl nitrite is

$$NO_3 + CH_3CHO \xrightarrow{k_{12}} HNO_3 + CH_3\dot{C}O \qquad (12)$$

comparable, such a reaction may compete in the present system, with acetone or isopropyl nitrate being the ultimate products. It seems possible, however, to rule out such a process on the basis of comparison of computed values of the maximum nitrogen trioxide quantum yields with the actual product quantum yields.

For nitrogen as a third body, the rate constant k_8 equals 3.2×10^{15} $l^2/mole^2\text{-}sec$.[17] For isopropyl nitrite as a third body, k_8 is probably about 3.2×10^{11} $l^2/mole^2\text{-}sec$, based on the estimated relative efficiencies of nitrogen and isopropyl nitrite as third bodies for iodine atom recombination.[17] Thus, the rate of step (8') is predicted to be about 5% of the rate of step (8) under typical experimental conditions and about 13% of the rate of step (8) under conditions favoring the third body reaction.

At an isopropyl nitrite pressure of 6.8 Torr and a nitrogen dioxide pressure of 0.08 Torr, the quantum yield of nitrogen trioxide is calculated to be about 3% of the quantum yield of acetone. Thus, even if every nitrogen trioxide molecule ultimately formed acetone, the amount of acetone formed from this source would be negligible compared to the amount formed by the disproportionation of isopropoxy radicals and nitrogen dioxide. At high nitrogen dioxide pressures, the quantum yield of nitrogen trioxide would be about 30% of the quantum yield of acetone. Again, assuming that every nitrogen trioxide molecule would react to produce acetone, the total amount of acetone would be approximately 30% higher than in the previous case. This is not experimentally observed and it is thus concluded that nitrogen trioxide does not react with isopropyl nitrite to form an appreciable amount of acetone.

Influence of Step (9)

It was shown earlier that step (9) cannot be ignored in interpretation of the data. No information on step (9) has been found in the literature. If the interpretation by Davidson and Thrush of the reaction of oxygen atoms

$$(CH_3)_2CHONO + O(^3P) \xrightarrow{k_9} CH_3COCH_3 + NO + HO \cdot \quad ? \qquad (9)$$

with methyl and ethyl nitrites is accepted, step (9) would be assumed to form acetone, nitric oxide, and hydroxy radical in a single step.[18] If this assumption is temporarily adopted, a steady state treatment of steps (1), (5)-(8), and (9) leads to:

$$\frac{R_{CH_3COCH_3}}{R_{(CH_3)_2CHONO_2}} = \frac{\phi_1' I_a' k_9[(CH_3)_2CHONO](1+k_8/k_9)}{\phi_1 I_a (k_8[NO_2]+k_9[(CH_3)_2CHONO])} + \frac{k_9}{k_5} \qquad (E)$$

where R = rate of formation of the product

ϕ_1, I_a = primary quantum yield and rate of light absorption of isopropyl nitrite

ϕ_1', I_a' = primary quantum yield and rate of light absorption of nitrogen dioxide

In this work, the yield ratio (acetone/isopropyl nitrate) has been associated with k_9/k_5. This is incorrect unless the first term in expression (E) is negligible with respect to 0.06. The magnitude of the first term depends critically on k_9, a quantity for which no value is available. Previously, a tentative value was presented assuming that the value for k_9 is

equal to the rate constant reported by Davidson and Thrush for the reaction of atomic oxygen with ethyl nitrite.[25] Limits for the value of k_9 may be fixed in the following sense. If k_9 is smaller than a certain lower limit, step (9) can have no effect on the yield ratio because the first term of expression (E) will be negligible. If k_9 is larger than a certain value, expression (E) predicts a variation in the ratio of rates of formation with variation of the pressure of either nitrogen dioxide or isopropyl nitrite that is not observed experimentally. In fact, if step (9) is to be significant for our results, the value of k_9 must lie between the value estimated from the work of Davidson and Thrush[25] and three times that value. Even if the value of k_9 fortuitously lies in this range, the effect of step (9) can be no greater than to make the reported value of k_5/k_6 20% too high.

There is another point of view that tentatively suggests that step (9) is not important in producing acetone in the present system. It is probably unrealistic to assume that k_9 for oxygen atom attack on isopropyl nitrite is the same as that for attack on ethyl nitrite. Davidson and Thrush[25] found that the Arrhenius parameters for oxygen atom attack on methyl and ethyl nitrites were the same as those determined for oxygen atom attack on primary and secondary hydrogen atoms of alkanes.[25] By extending this analysis to isopropyl nitrite, it is found that k_9 is predicted to be about 6.4×10^7 ℓ/mole-sec. This value, if substituted into expression (E), leads to a prediction of a large variation in the yield ratio. Under the experimental conditions of this work, no such variation has been observed. One may then speculate that the $(CH_3)_2CHO$ radical formed initially in step (9) does not inevitably form acetone under the experimental conditions even though decomposition of this radical is certainly exothermic.[25]

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